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EXECUTIVE SUMMARY

STATUS REPORT ON ULTRASONIC MEASUREMENT OF HYDRIDE PLATELET CONCENTRATION IN Zr-Nb PRESSURE TUBES

Absorption of hydrogen or deuterium to form zirconium hydride platelets is becoming the life-limiting factor for Zr-Nb pressure tubes. These hydride platelets precipitate in the the circumferential-axial plane in the bulk of the tube, or the radial-axial plane in the rolled joint region. Most information on the rate of hydride platelet formation is obtained from tube removal, and there is a pressing need for an in-service nondestructive measurement technique. This report describes the progress towards developing an ultrasonic method.

The most spectacular result to date has been the imaging of individual platelets using a Scanning Acoustic Microscope at 370 MHz in defocussed mode.These images appear to be formed by differences in velocity between the hydride platelets and the matrix. However, this technique is likely to be impractical for in-service use. Small velocity changes have been observed using longitudinal and surface waves, which may provide a better basis for an in-service measurement system. Ultrasonic spectroscopy and attenuation, and nuclear acoustic resonance have been rejected as potential techniques.

Future directions will involve measuring velocity changes in hydrided and unhydrided regions of the same specimen using a number of different wave modes. The objective will be to determine which wave modes are most affected by the presence of hydrides. Most of the work will be done externally, and interesting results replicated at OHRD where possible.

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STATUS REPORT ON ULTRASONIC MEASUREMENT OF HYDRIDE PLATELET CONCENTRATION IN Zr-Nb PRESSURE TUBES

ABSTRACT

This report summarizes the progress during the last year towards developing an ultrasonic technique for measuring hydride concentrations in CANDU reactor pressure tubes. By far the most spectacular result is the imaging of platelets using a scanning acoustic microscope at 370 MHz. However, small changes of velocity have been observed using longitudinal and surface waves, which could prove more useful for a practical in-service measurement system. Ultrasonic spectroscopy and attenuation, and nuclear acoustic resonance have been rejected as potential techniques. Future research directions are outlined.

1.0 INTRODUCTION

1.1 The Problem

CANDU reactor pressure tubes, currently made from Zr-2.5%Nb, absorb hydrogen (or deuterium) during in-service operation. The H or D is dissolved in solid solution, and precipitates as hydrides or deuterides (henceforth called hydrides) when saturation is reached, or temperatures are lowered. The hydrides form as flat platelets, typically in the circumferential-axial plane. The hydride platelets can re-orient due to applied stresses, and become radial-axial in the rolled joint region.

The precipitation of hydrides has been instrumental in recent pressure tube problems: hydride blistering in Pickering 1 and 2, delayed hydride cracking in Pickering 3 and 4, and delayed hydride cracking from a manufacturing defect in Bruce 2, N06. Overall, absorption of deuterium is becoming an expensive problem, and may dictate the usable life of CANDU pressure tubes.

The deuterium pick-up problem has been described by Warr/1/. At this stage, most of the information comes from pressure tubes removed from reactors, and as such gives a snapshot rather than a continuous history. Furthermore, only a few Zr-Nb tubes have been removed to date so data is very limited, and ambiguous. For example, it is not clear whether the all-important deuterium absorption rate follows a linear law, or if "breakaway" absorption occurs, as with the Pickering 1 and 2 Zircalloy-II pressure tubes.

Thus, there is a very strong need for more information on deuterium absorption rates in-reactor on a regular basis. Essentially this means developing a nondestructive testing technique for in-service use. Of the potential techniques, ultrasonics is a strong candidate for measuring hydride concentrations in reactor because:

1) ultrasonics is primarily a volumetric test technique, rather than a surface technique;

2) it can be used for characterizing materials; and

3) it is routinely used for pressure tube inspections.

This report summarizes the progress to date in developing an ultrasonic technique for measuring hydride platelet concentration for in-reactor use.

1.2 Project Management Philosophy

The behaviour of zirconium in high temperature, high radiation corrosive environments is not fully understood/1/, though considerable research has recently been performed/2,3,4/. For example, more than one bulk hydride platelet morphology has been observed, and the platelet orientation is not always perfectly circumferential-axial/5/. It has been difficult to obtain much useful information from basic ultrasonic studies on pure hydride, though limited work has been done. Furthermore, large pieces of hydride may not be fully representative of in-service platelets. Thus the emphasis has been on preparing closely-controlled specimens, representative of in-service material, rather than on basic research.

As a result, an empirical experimental philosophy has been followed, with appropriate ultrasonic techniques being tested on suitable specimens. Since much of the technology required has been highly specialized, most of the research has been sub-contracted to outside organizations. There has also been a policy of trying to reproduce interesting externally generated results within OHRD, since the changes in material properties being sought are typically very small, and misleading results can be caused by, for example, poor surface finish or non-parallel specimen sides.

This report initially describes previous work on measuring hydride platelet concentration in pressure tubes (up till May 1986), then summarizes results obtained within the last year. Future prospects are then discussed.

2.0 PREVIOUS WORK ON HYDRIDE CONCENTRATION MEASUREMENTS

2.1 Ultrasonic Techniques

Initial work by Bussiere et al/6/ at NRC-IMRI on a variety of specimens of various hydride concentrations showed no detectable changes due to the presence of hydrides at frequencies up to 50 MHz, temperatures up to 400 degrees C, or with a Scanning Acoustic Microscope (SAM) up to 450 MHz. Patel/7/ at McMaster University generated attenuation contours at relatively low frequencies using continuous wave ultrasonics. The "ridges" detected were subsequently thought to be due to surface finish, and recent re-scanning of the specimens has been more productive (see Sections 3.2 and 3.4 below).

Smith/8/ at UKAEA Harwell performed high frequency (70 MHz) spectral analysis on specially prepared specimens, but no trend was observed. Kramer/9/ at OHRD performed similar tests in immersion, also with no success. Other SAM work by VG Semicon in the UK/10/ detected no differences between hydrided and unhydrided areas.

OHRD have prepared carefully-made, flat, fairly smooth specimens with hydride (typically 200 ppm) at one end, and as-received (unhydrided) material at the other. These specimens have been very useful as they have eliminated many variables, such as metallurgical effects. Allen at OHRD performed ultrasonic tests on samples of pure ZrH_x ($x = 1.63$ or 1.7), which showed that the acoustic impedance mismatch between Zr and ZrH_x was only about 5% using longitudinal waves, but around one third using shear waves. This and other results have tended to move the research efforts towards shear wave from longitudinal wave testing.

Moles/11/ tested a specially prepared hydrided specimen using a Scanning Laser Acoustic Microscope (SLAM) at frequencies up to 100 MHz. Small differences in attenuation were observed between hydrided and unhydrided regions for longitudinal waves. Using shear waves, different orientations showed different trends, ie. the hydrided regions showed higher attenuation in one orientation and lower attenuation when the specimen was rotated 90 degrees. The differences were small but reproducible, suggesting different behaviour for different shear wave modes. A SAM inspection at 150 MHz showed no detectable difference between hydrided and unhydrided areas.

2.2 Other Techniques

Due to the importance of the hydride-absorption problem to the CANDU system, a number of other techniques besides ultrasonics are being investigated for measuring hydride platelet concentration in pressure tubes. Bussiere et al/6/ have looked at resistivity approaches, as has Tashiro/12/, with some success.

Harwell and Aerotest Operations in California neutron radiographed flat and curved specimens, though neither could detect hydrides at concentrations up to 400 ppm. Chalk River Nuclear Laboratories have been interested in developing an eddy current technique. More recently, Sundfors at Washington University has tested a Zr-Nb block using Nuclear Acoustic Resonance (which is the little-used ultrasonic analog to Nuclear Magnetic Resonance), but with no success/13/.

3.0 CURRENT RESULTS

This section describes the ultrasonic results obtained during the last year, since/11/ was written. The results are described by the ultrasonic technique used.

3.1 Scanning Acoustic Microscopy

Oxford University/14/, as part of the second Harwell spectral analysis contract, performed high frequency (370 MHz) acoustic microscopy on a 400 ppm specimen. In contrast to the three previous workers/6,10,11/, Oxford used a "defocussed" technique, which meant that the SAM was generating and receiving re-radiated surface waves (see Figure 1). The results were most impressive. Figures 2, 3 and 4 show SAM images of the as-received, an intermediate level (precise concentration unknown) and the 400 ppm material. The hydrides are clearly visible, particularly in Figure 3, which is probably around the hydride levels of interest (50 - 100 ppm).

This surface-wave imaging technique relies on differences in velocity between the various components of the material to cause constructive or destructive interference of the surface waves. These velocity differences could be caused by the anticipated differences in velocity between the hydride platelets and the parent plate, or by local residual stresses straining the lattice.

Since the density difference between the platelets and parent plate is about 14%, a similar difference in acoustic velocity should occur for longitudinal waves, but in the opposite direction (hydrides have lower density and therefore higher velocity). The difference should be greater for shear waves due to the greater difference in acoustic impedance. (To confuse the issue, surface waves contain both shear and longitudinal components). However, the 14% increase in volume on precipitation of hydride platelets could cause a significant increase in local stresses, which could also affect wave velocity.

Despite the spectacular images in Figures 3 and 4, a SAM technique is unlikely to be optimum for several reasons:

1) it would be difficult to put a SAM down a pressure tube;

2) at 370 MHz, wavelengths are about 4 microns. Since surface waves only penetrate the top 1-2 wavelengths, the SAM technique could not read through the oxide layer in most cases;

3) currently we cannot estimate the hydride concentration from circumferential-axial plane images, though this could probably be remedied; and

4) the near-oxide hydride layer may not be fully representative of the bulk.

3.2 Velocity Measurements

Smith et al/14/ also performed surface (or Raleigh) wave velocity measurements on the hydride samples. Typical results are shown in Table 1 and Figure 5. While there is considerable scatter, primarily due to differences in texture and local microstructure, there is a distinct trend with velocity increasing with increasing hydride concentration. Again, surface waves only operate within the top 1-2 wavelengths of the

surface, so the results may not be fully representative of the bulk. Also, surface waves have both shear and longitudinal components, further complicating interpretation.

Patel/15/ has measured longitudinal wave through-thickness velocity, and detected a 0.4% increase in velocity in the hydrided area. A velocity increase of this order is not unexpected for a 200 ppm concentration with a 14% increase in velocity if one assumes that the hydride has an isotropic effect on velocity (which seems unlikely since the distribution is highly anisotropic – see Section 4.0). Patel's results are shown in Figure 6.

The longitudinal wave velocity experiment was repeated at OHRD on another specimen. While a slightly different percentage change in velocity was measured, the general effect of hydrides on longitudinal wave velocity was supported. Further work is anticipated to clear up the discrepancies, especially since the experimental errors are not much smaller than the changes being measured. Nevertheless, both Smith's and Patel's velocity results are encouraging and offer potential.

3.3 Spectral Analysis

Smith/14/ performed high frequency, immersion longitudinal and shear wave spectral analysis on hydrided and unhydrided regions. In both cases there was no significant difference between the spectra. The results were repeated by Kramer/9/ at OHRD, with the same result. Moles/16/ performed longitudinal wave spectral analysis at several frequencies on re-oriented hydrides, also with no detectable differences.

3.4 Attenuation Measurements

Smith/14/ performed attenuation tests on hydrided and unhydrided areas using surface waves, as shown in Table 1. There is some scatter as expected, but the trend shows the attenuation is typically highest at the intermediate hydride levels. This is contrary to intuitive predictions, but the changes are small. Attenuation measurements generally are affected by many variables such as surface finish, grain size, texture, hardness, local composition, and are not a particularly good method for characterizing metals in many cases.

Patel/15/ measured attenuation using through-thickness longitudinal waves, and found a small but consistent trend, with values about 10% higher for the hydrided region. OHRD work had shown no significant difference between the hydrided and unhydrided regions on similar specimens. Despite Patel's results, attenuation measurements are not considered a desirable approach for hydride concentration measurements.

4.0 DISCUSSION

The Oxford University SAM images have been the most exotic results to date, and the pictures of hydrides are very confidence-inspiring. However, the technique is not likely to be of much use in service (see Section 3.1). Spectroscopy has been unsuccessful, which is disappointing as it would have been relatively easy to apply in-reactor. Despite some mildly encouraging attenuation results, changes in attenuation can be caused by so many factors that the technique is not recommended.

The best prospects lie with a series of velocity measurements. Typically, velocity can be measured to high accuracy, so small changes are detectable. Because of the many unknowns in pressure tubes (wall thickness, oxide thickness, ovality, texture/17/, microstructure, composition), a single velocity measurement would almost certainly be insufficient. The hydrides in Zr–Nb form in a two–dimensional plane in a three dimensional matrix, ie, they are highly anisotropic. Consequently, it is reasonable to hope that different wave modes will be affected to different degrees by the presence of hydrides.

Conveniently, there has been a continuing interest in the application of ultrasonic velocity changes for measuring applied and residual stress in metals. Typically, stress has a very small effect on ultrasonic velocity, of the order of the changes observed by Smith and Patel, or smaller. But different wave modes are affected by different amounts for a given stress level. Consequently, stress measurement techniques have concentrated on sending two waves of different modes (eg. shear waves polarized in two different directions) down the same path, and measuring small velocity differences/18/. This technique can eliminate the effects of microstructure and texture, which remain constant. This general approach may be applicable to hydride platelet concentration measurements.

5.0 FUTURE DIRECTIONS

The work to date can be summarized by saying that the ultrasonic technique which offers the best prospects at the moment is the accurate velocity measurement of two wave modes travelling over identical paths, one of which is more affected by hydride concentration than the other. The CANDEV funding for this project is largely being spent with the objective of determining which wave modes are most affected by hydrides. Unfortunately, generating the appropriate waves can be difficult in many cases. Based on this logic pattern, the following projects are in progress or have been initiated:

1) Hutchins at Queen's University will perform velocity measurements using two polarized shear waves generated by laser ultrasonics.

2) Magnasonics in New Mexico will perform velocity measurements using circumferential–direction, axially–polarized shear waves generated by an EMAT device.

3) Patel will perform velocity and attenuation measurements using conventional PZT–generated shear waves.

4) Smith will perform further surface wave velocity measurements.

In addition, Smith will perform further SAM work to determine if lower frequencies could be used. Cheeke at Sherbrooke University may also perform some SAM work with a similar objective in mind.

Overall, the ultrasonic results obtained in the last year have been encouraging. Hopefully the new emphasis on velocity will indicate which waves are most suitable for the purpose of measuring hydride concentration, and thus point towards a technique for in–reactor measurement.

A word of caution should be given. Ultrasonic residual stress measurements have been investigated for some time, but the in-service application has been difficult due to the small velocity changes and the number of variables. However, Zr-Nb pressure tubes are a very specific composition and geometry, so some of these general problems may be reduced. Nevertheless, the velocity changes from hydrides are small, typically one tenth of those from texture.

6.0 CONCLUSIONS

1. Scanning acoustic microscopy at 370 MHz has successfully imaged hydrides using re-radiated surface waves.

2. Velocity measurements using longitudinal and surface waves have shown higher velocities with increasing hydride content.

3. Spectral analysis, neutron radiography and nuclear acoustic resonance are not potential techniques for hydride concentration measurement.

4. Attenuation measurements may show some differences, but the number of sources of error are too large for this to be considered a reliable technique.

5. Overall, the results to date can be summarized as saying significant progress has been made in the last year.

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REFERENCES

1. B.D. Warr, OHRD Report No. 87-73-K, May 19, 1987.

2. V.F. Urbanic, Sixth International Symposium on Zirconium in the Nuclear Industry, ASTM STP 824, Ed. D.G. Franklin and R.B. Adamson, American Society for Testing and Materials, 1984, p. 554.

3. C.E. Coleman, B.A. Cheadle, J.F.R. Ambler, P.C. Lichtenberger and R.L. Eadie, Canadian Metallurgical Quarterly, Vol. 24, 1985, p.245.

4. R.G. Fleck, E.G. Price and B.A. Cheadle, see ref. 2, p. 88.

5. G.K. Shek, private communication.

6. J. Bussiere et al., IMRI-NRC, Project 401, Progress Report #1, October 1, 1983 to March 31, 1984.

7. N.D. Patel, private communication.

8. R.L. Smith, AERE Report No. G3883, April 1986.

9. S.M. Kramer - unpublished results.

10. VG Semicon Report on Low Frequency ASM 100 of Hydrided Zirconium, 1986.

11. M.D.C. Moles, OHRD Report No. M86-74-K, July 17, 1986.

12. K.M. Tashiro, OHRD Report No. 87-41-K.

13. R.K. Sundfors, private communication.

14. R.L. Smith, M.J. Crook, G.A.D. Briggs and P.R. Harrison, Harwell AERE Report No. G 4222, May 1987.

15. P.S. Nicholson, N.D. Patel and J. van den Andel, Interim Report on Phase I of Attenuation Studies in Zr-Nb, July 1987.

16. M.D.C. Moles - unpublished results.

17. T. Konshi and M. Honji, see ref no. 2, p. 256.

18. D.R. Allen, W.H.B. Cooper, C.M. Sayers and M.G. Silk, Research Techniques in NonDestructive Testing, Vol. 6, Ed. R.S. Sharpe, 1982, p. 151.

TABLE 1

Rayleigh Wave Velocity and Attenuation Measurements/14/

Measurements were made at three points along the length of each specimen (except in the case of specimen 6, in which only one measurement was made). In the following table, the designation indicates propagation perpendicular to the long axis of the specimen, and 9 parallel. Units of velocity are ms^{-1}, and of attenuation are Napers per reciprocal wave number.

Specimen (1–2)	Velocity ms^{-1}	Attenuation $Np^{-1} \times 10^{-1}$
A	2219.9	0.2132
B	2221.5	0.2048
C	2208.8	0.2031
A9	2140.1	0.1745
B9	2142.4	0.1642
C9	2144.1	0.1746
Specimen (3–4)		
A	2224.6	0.2104
B	2224.8	0.2072
C	2223.6	0.2001
A9	2140.7	0.1726
B9	2146.1	0.1796
C9	2144.8	0.1826
Specimen (5–6)		
A	2233.3	0.1932
B	2227.4	0.1996
C	2229.0	0.2056
A9	2148.6	0.1837
B9	2149.7	0.1706
C9	2147.9	0.1718

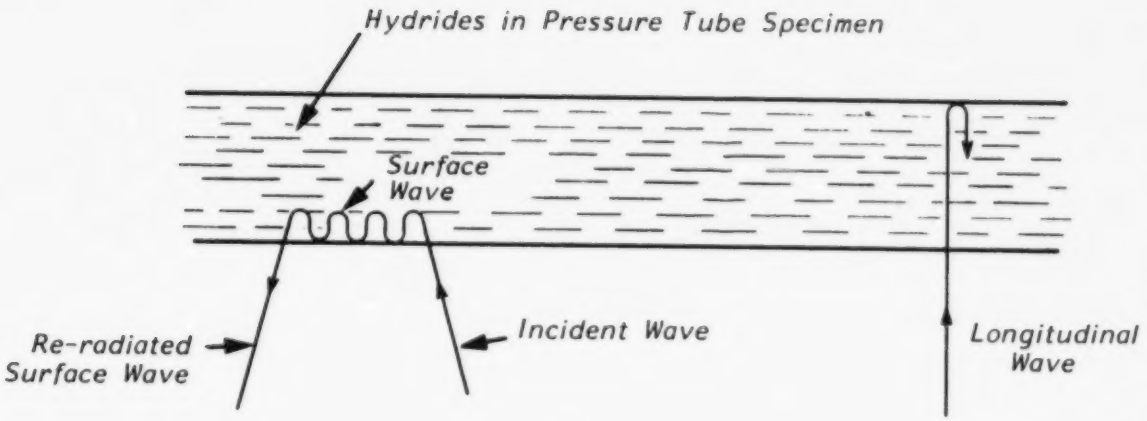

FIGURE 1

SCHEMATIC SHOWING PROPAGATION OF SURFACE AND LONGITUDINAL WAVES IN HYDRIDED SPECIMEN

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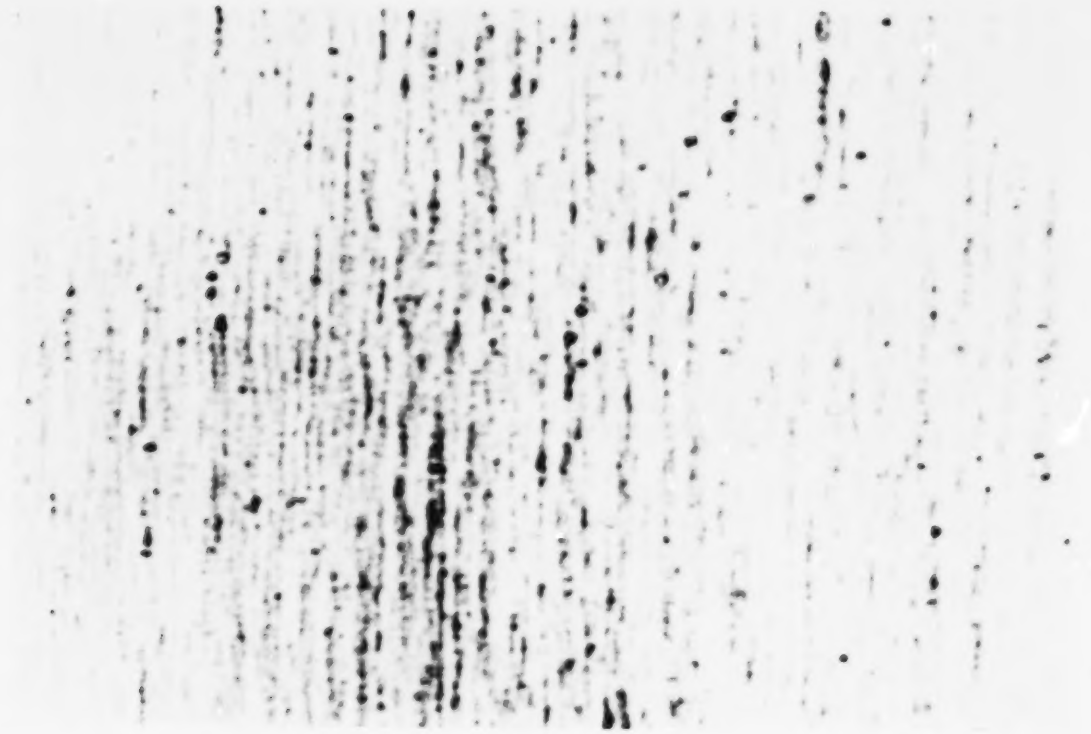


FIGURE 2
SCANNING ACOUSTIC MICROGRAPH OF AS-RECEIVED AREA, SHOWING PRIMARILY SURFACE CONTRAST (DEFOCUSSED, 370 MHz)

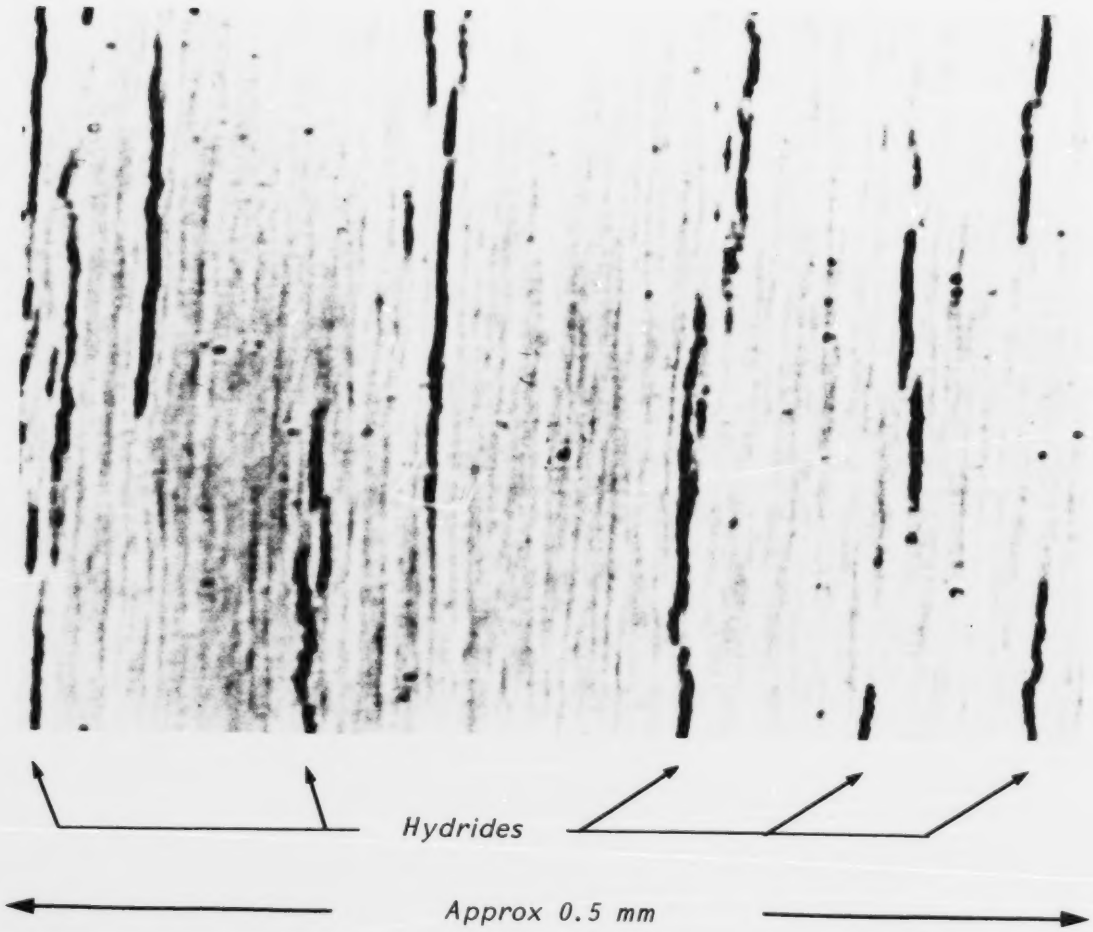
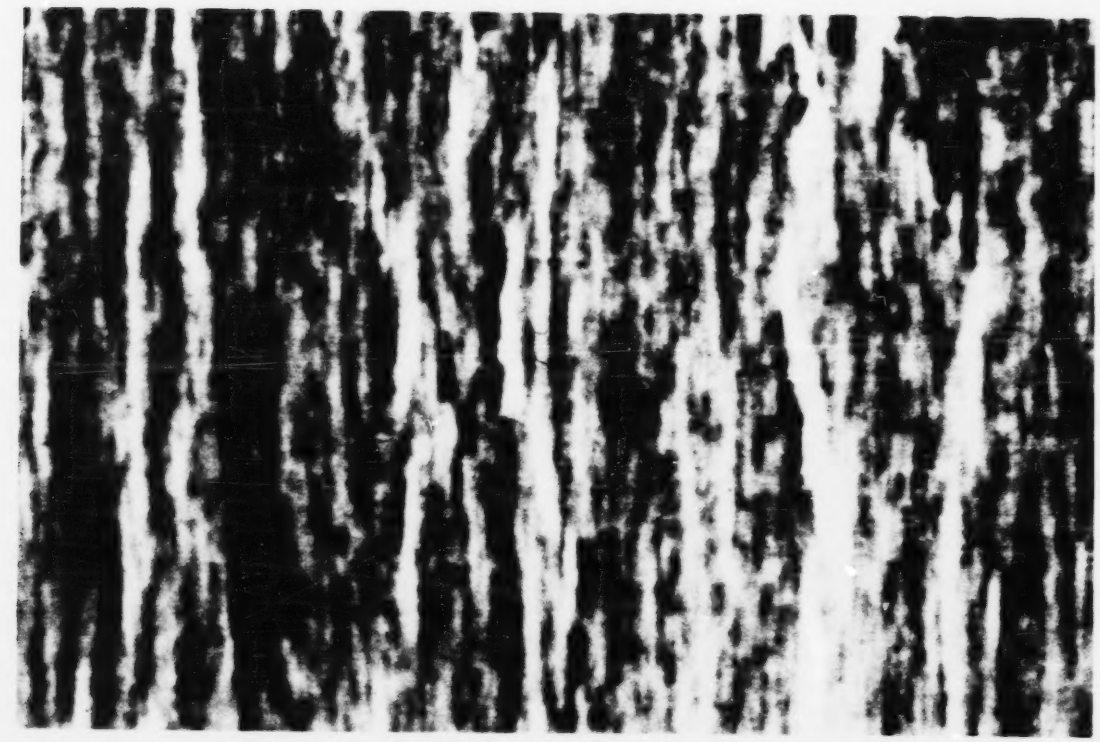


FIGURE 3
SCANNING ACOUSTIC MICROGRAPH OF INTERMEDIATE HYDRIDE CONCENTRATION AREA, SHOWING IMAGES OF HYDRIDES (DEFOCUSSED, 370 MHz)

175364-RD



Approx 0.5 mm

FIGURE 4

SCANNING ACOUSTIC MICROGRAPH OF HIGH HYDRIDE CONCENTRATION AREA, SHOWING MULTIPLE HYDRIDE PLATELETS (370 MHz, DEFOCUSSED)

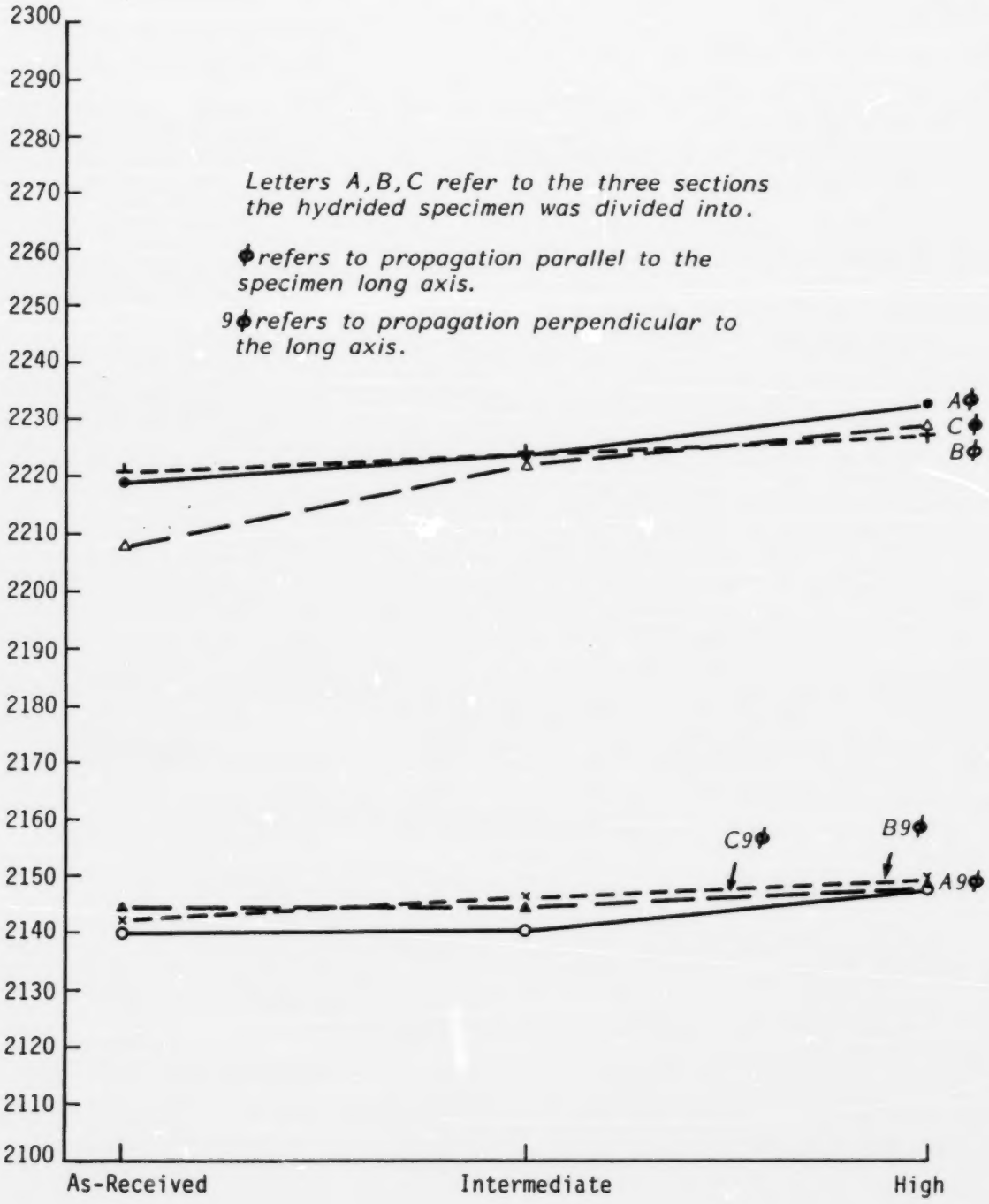


FIGURE 5
PLOT OF VELOCITY VS HYDRIDE CONCENTRATION
FOR SURFACE WAVES/14/

175366-RD

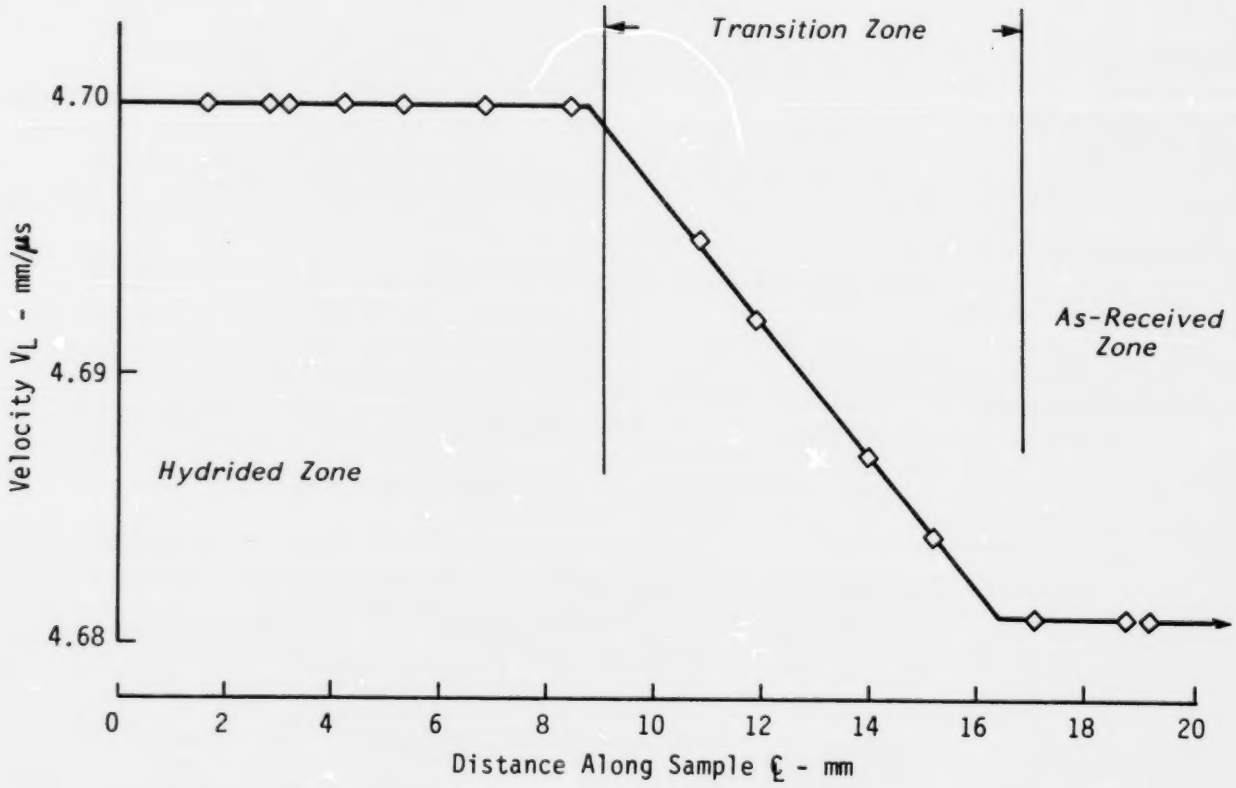


FIGURE 6
VELOCITY CHANGE AT 40 MHz DUE TO HYDRIDING

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